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<p>(54) Title: IMPROVEMENTS IN OR RELATING TO NON-WOVEN FIBROUS MATERIALS</p> <p>(57) Abstract</p> <p>A binding composition for non-woven fibrous materials comprises a copolymer emulsion based on at least 30 % by weight vinyl alkanoate and uses N-(n-butoxymethyl) acrylamide (NBMA) as post polymerisation cross-linking agent to reduce formaldehyde emission.</p>		

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Title: Improvements in or relating to non-woven  
fibrous materials

Field of the invention

This invention relates to non-woven fibrous materials, and concerns a binding composition intended for use in binding non-woven fibrous materials, for example paper and viscose, use of the binding composition and the resulting product.

Background to the invention

Non-woven fibrous material comprises a consolidated mass of fibres which may be laid down by mechanical, chemical, pneumatic, electrical or vacuum means and deposited in a desired flat shape, for example as webs, mats or sheets, or in a three dimensional form. The fibres may be natural or synthetic or a combination. In general the fibres to be used will be selected to suit the desired end use of the non-woven product. Thus fibres may be derived from wood, i.e. cellulose, or may be cotton, glass, asbestos, rayon, wool, viscose etc. The fibres may be deposited in a random manner, or may be positioned or aligned along particular axes. The non-woven product may contain layers of fibre oriented in a cross-layered manner to provide a uniform strength across the product.

Usually it is necessary to submit the product to a binding step to ensure the product maintains its physical integrity.

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One route to binding the product is to introduce a binding composition during or after formation of the product. Some of the binding composition will coat the fibres but a portion will be concentrated at the positions where the fibres touch. Subsequent treatment, usually by the application of heat, dries the binding composition and gives structural integrity to the product. The non-woven product may be impregnated with the binding agent by dipping or immersing the fabric in the agent to provide sufficient pick-up. The wetted non-woven product in a form of a web can then be passed between a pair of pressure rollers to ensure the impregnation is uniform and so to control the amount of binding agent applied. In general there is no restriction on the means of application of the binding composition and this may be by, e.g. dipping, soaking or spraying. Bound non-woven fibre products are useful e.g. as curtains, in furniture, as drapes, filters, packaging, wiping cloths, fabric interlining for clothes, and industrial sealing material such as gaskets. A particular market is in the use of non-woven padding as absorbents in, e.g., babies nappies (diapers), female sanitary products etc.

It is well known to use copolymer emulsions as binding compositions for non-woven fibrous materials. A particularly suitable base for binding compositions is copolymer emulsions obtained by polymerising unsaturated monomers in an emulsion system. Suitable copolymer emulsions may be obtained by means of processes performed at ambient pressure or under elevated pressure, e.g. up to 120 bars. Copolymer emulsion compositions suitable for this purpose will usually contain a monomer capable of cross-linking in a post-polymerisation step. Thus the copolymer emulsion will be applied to the non-woven product and first

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subjected to heating to remove the water. Then in a further heating step the cross-linkable monomer cross-links to provide a three dimensional copolymer network with strength sufficient to provide structural integrity.

The cross-linkable monomer used is required to have an appropriate cross-linking efficiency, appropriate wet and dry strengths and, where appropriate, sufficient tensile strength when the resulting non-woven product is subjected to solvent or other chemical contact. Additionally there has been a general desire to reduce the content of formaldehyde in some non-woven products, in particular those designed for human contact e.g. babies nappies.

Formaldehyde may be present in the fibrous components of the non-woven product and may also be generated by the cross-linking reaction. For example, one cross-linkable monomer widely used for this purpose is N-methylolacrylamide (NMA), but the cross-linking reaction of this monomer generates formaldehyde.

#### Summary of the invention

In one aspect of the present invention provides a binding composition for non-woven fibrous materials, comprising a copolymer emulsion in which at least about 30% by weight of the monomer content is vinyl C1 to C4 alkanolate and an amount of N-(n-butoxymethyl) acrylamide effective to act as a post polymerisation cross-linking agent is present.

By using N-(n-butoxymethyl) acrylamide (NBMA) as the post-polymerisation cross-linking monomer in place of NMA in a binding composition for non-woven fibrous materials, it is possible to produce non-woven fibrous products having reduced levels of formaldehyde.

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The copolymer emulsion solids are required to include an amount of the cross-linkable monomer (NBMA) effective to provide the necessary strengthening of the copolymer solids and thereby structural integrity of the non-woven body. Usually the effective amount of cross-linkable monomer will be from about 0.5% to about 10% by weight, typically below about 5% by weight, of the total monomer content.

Preferably not more than 90% by weight, more preferably between 60 and 80% by weight, of the monomer content is vinyl C1 to C4 alkanate, with the preferred material being vinyl acetate.

The copolymer emulsion may include a C2 to C4 alkylene monomer, e.g., ethylene, typically in an amount from 5% to 40% by weight of total monomer.

Another possible comonomer is selected from the alkyl (C2 to C10) (meth) acrylate class e.g., butylacrylate or 2 ethyl hexyl acrylate, which will preferably be present in an amount of from about 10% to about 60% by weight of total monomer.

A further class of possible functional comonomer is carboxyl group-containing monomers, e.g. acrylic acid, methacrylic acid, crotonic acid, itaconic acid etc.

Hydroxy alkyl (meth) acrylate monomers, e.g. hydroxy ethyl acrylate, may also be included,

Sodium vinyl sulphonate and acrylamide are further examples of functional monomers that may be included. In particular, use of sodium vinyl sulphonate has been found useful for

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improving mechanical stability of the composition in use and so providing good runnability.

These further monomer materials would typically be included in amounts of up to 5% by weight of total monomer.

One or more surfactants (non-ionic or ionic) may be included as appropriate.

The copolymer emulsion can be prepared using generally conventional techniques, which are well known and well characterised in the literature. Polymer synthesis (vols I & II) by Sandler & Karo (Academic Press 1974) and Preparative Methods of Polymer Chemistry (2nd Ed) by Sorensen & Campbell (Interscience 1968) provide preparative information. Methoden der Organischen Chemie (Houben-Weyl) Band XIV published by Georg Thieme Verlag Stuttgart (1961) also provides preparative descriptions.

Any suitable initiator system can be used, but it is preferred not to use formosul (sodium formaldehyde sulphonylate) as this produces formaldehyde. It is preferred to use a thermal polymerisation, with no reducing agent, e.g. using ammonium or alkali metal persulphates. Redox initiation may also be used, with a persulphate, hydrogen peroxide or an organic peroxide as the oxidising agent and with the reducing agent typically being ascorbic acid or sodium metabisulphite.

The binding composition of the invention can be used for binding non-woven fibrous materials in generally conventional manner, e.g. by dipping, soaking, or spraying or by use of rollers and a bath.



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Thus, in a further aspect the present invention provides a process of binding a non-woven fibrous material, comprising impregnating the material with a binding composition in accordance with the invention; drying the copolymer emulsion; and subjecting the impregnated material to thermal treatment to provide cross-linking.

The invention also includes within its scope the resulting non-woven fibrous material or product.

#### Detailed description of the Invention

The invention will be further described by way of illustration in the following Examples.

#### Test Methods

Viscosity: This was measured in centipoise using a Brookfield viscometer (ERV type) at 25°C with spindle 2 at 20 rpm.

Tensile Strength: This was measured for dry, wet and solvent (acetone) treated samples using a Lloyd Tensometer. Latices were diluted to 20% solids and impregnated on to Whatman's No. 4 filter paper and viscose web of weight 30 g/m<sup>2</sup> for Examples 1 to 4 and weight 15 g/m<sup>2</sup> for Examples 5 to 10. The solids pick-up was 20%. The cross-linking reaction was catalysed by citric acid, (1% w/w on polymer solids for Examples 1 to 8 and 10, 2% w/w for Example 9). Curing was at 165°C on a rotary iron for 12 seconds for filter paper and light viscose web and 24 seconds for heavy viscose web. Strips of impregnated substrate of dimensions 200 x 50 mm were stretched at a speed of 100 mms<sup>-1</sup>. The breaking load, F, in Newtons, (N),



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and the strain, (e as %), at break were measured.

Formaldehyde Content (in ppm): A 1g sample of impregnated substrate was extracted with deionised water, (20ml), for 1 hour at 40°C and then filtered. 1.0ml of the extract was diluted with 2.7ml of water, then 0.3ml of a 1% w/v chromotropic acid solution and 6.0ml of conc. sulphuric acid were added. The solution was cooled and the 580nm absorption was measured.

#### Example 1

A solution of ferric ions, (1.4g of a 0.1% solution), in 146.5g of deionised water was purged with nitrogen for 30 minutes in a 700ml stirred vessel. A slow nitrogen purge was continued throughout the polymerisation. A surfactant solution consisting of 16.0g of Synperonic NP30, (70% active), and 0.56g of Gafac RE610 in 80.0g of water plus 2.58g of 1N sodium hydroxide solution was prepared. 10% of this surfactant solution was added to the reactor. (Synperonic NP30 is nonylphenol 30 EO (30 ethylene oxide units) obtainable from Cargo Fleet Chemicals, and Gafac RE610 is phosphate ester obtainable from Gaf (Great Britain) Co. Ltd., of Manchester, England.) A monomer mixture consisting of 14.0g of vinyl acetate, 12.9g of n-butyl acrylate and 0.28g of an 80/20 methacrylic acid/methyl methacrylate blend was charged to the reactor. Solutions of sodium persulphate, (0.34g in 1.66g of water), and sodium metabisulphite, (0.23g in 1.67g of water), were added to the reactor and the temperature was raised to 50°C. After 5 minutes at 50°C slow additions of the remaining 90% of surfactant solution, a monomer mixture consisting of 126.0g of vinyl acetate, 115.9g of n-butyl acrylate, 9.23g of N-(n-butoxymethyl) acrylamide (NBMA) and 2.52g of 80/20

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methacrylic acid/methyl methacrylate mix, and catalyst solutions comprising 2.58g of sodium persulphate in 25.0g of water and 1.57g of sodium metabisulphite in 25.0g of water, were begun to last for 2 hours at constant rate. When the slow additions were complete the temperature was held at 50°C for 15 minutes. The temperature was reduced to 45°C, 0.34g of t-butylhydroperoxide was added, followed by a solution of sodium metabisulphite, (0.34g in 1.66g of water). The medium was allowed to exotherm to 50°C, maintained there for 15 minutes and then cooled. The pH was adjusted to 4.5-5.0 with ammonia and the emulsion was filtered through 250 mesh nylon to remove any coagulum. This resulted in a latex with a solids content of 49.01% and a viscosity of 42 centipoise, measured as described above.

#### Example 2

The example used the procedure of Example 1 except that sodium metabisulphite was replaced by sodium tartrate, to produce a latex with a solids content of 45.53% and a viscosity of 40 centipoise.

#### Example 3

A surfactant solution consisting of 16.0g of Synperonic NP30, (70% active), and 0.56g of Gafac RE610 in 80.0g of water plus 2.58g of 1N sodium hydroxide solution was prepared. 10% of this surfactant solution was added to a 700ml reactor containing 146.5g of deionised water. A monomer mixture consisting of 14.0g of vinyl acetate, 12.9g of n-butyl acrylate and 0.28g of an 80/20 methacrylic acid/methyl methacrylate blend was charged to the reactor. A solution of sodium persulphate, (0.34g in 3.0g of water), was added to the reactor and the temperature was raised to

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75°C. After 5 minutes at 75°C slow additions of the remaining 90% of surfactant solution, a monomer mixture consisting of 126.0g of vinyl acetate, 115.9g of n-butyl acrylate, 9.23g of N-(n-butoxymethyl) acrylamide and 2.52g of 80/20 methacrylic acid/methyl methacrylate mix, and a catalyst solution consisting of 2.58g of sodium persulphate in 50.0g of water, were begun to last for 2 hours at a constant rate. When the slow additions were complete the temperature was held at 75°C for 15 minutes. The temperature was reduced to 45°C, 0.34g of t-butylhydroperoxide was added, followed by a solution of sodium metabisulphite, (0.34g in 1.66g of water). The medium was allowed to exotherm to 50°C, maintained there for 15 minutes and then cooled. The pH was adjusted to 4.5-5.0 with ammonia and the emulsion was filtered through 250 mesh nylon to remove any coagulum. This resulted in a latex with a solids content of 49.42% and a viscosity of 31 centipoise.

#### Example 4

This is a comparative example, using N-methyloacrylamide (NMA) as the cross-linking monomer in place of NBMA. A solution of ferric ions, (1.4g of a 0.1% solution) in 136.2g of deionised water was purged with nitrogen for 30 minutes in a 700ml stirred vessel. A slow nitrogen purge was continued throughout the polymerisation. A surfactant solution consisting of 16.0g of Synperonic NP30, (70% active), and 0.56g of Gafac RE610 in 80.0g of water plus 2.58g of 1N sodium hydroxide solution was prepared. 10% of this surfactant solution was added to the reactor. 18.7g of a 45% aqueous solution of N-methyloacrylamide was added to the remaining 90% of the surfactant solution. A monomer mixture consisting of 14.0g of vinyl acetate, 12.9g of n-

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butyl acrylate and 0.28g of an 80/20 methacrylic acid/methyl methacrylate blend was charged to the reactor. Solutions of sodium persulphate, (0.34g in 1.66g of water), and formosul, (0.23g in 1.67g of water), were added to the reactor. When an exotherm was evident, after 5 minutes, slow additions of the NMA/surfactant solution, a monomer mixture consisting of 126.0g of vinyl acetate, 115.9g of n-butyl acrylate and 2.52g of 80/20 methacrylic acid/methyl methacrylate mix, and catalyst solutions comprising 2.58g of sodium persulphate in 25.0g of water and 1.57g of formosul in 25.0g of water, were begun to last for 2 hours at a constant rate. The temperature was raised to 50°C during the first 15 minutes of these additions. When the slow additions were complete the temperature was held at 50°C for 15 minutes. The temperature was reduced to 45°C, 0.34g of t-butylhydroperoxide was added, followed by a solution of formosul, (0.34g in 1.66g of water). The medium was allowed to exotherm to 50°C, maintained there for 15 minutes and then cooled. The pH was adjusted to 4.5-5.0 with ammonia and the emulsion was filtered through 250 mesh nylon to remove any coagulum. This resulted in a latex with a solids content of 49.17% and a viscosity of 146 centipoise.

#### Example 5

A solution of 103g of Synperonic NP30, (70% active), in 750g of deionised water and a monomer mixture consisting of 67g of vinyl acetate and 0.45g of acrylic acid were charged to a 4 litre stainless steel reactor. The temperature was raised to 30°C, then the reactor was purged twice with nitrogen and once with ethylene. The reactor was charged with ethylene to a pressure 52 bar, and then heated to a temperature of 70°C. At this temperature 10% of a solution of sodium persulphate, (7.5g in 300g of water), was added to the

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reactor. A monomer mixture consisting of 1294g of vinyl acetate, 30.0g of N-(n-butoxymethyl) acrylamide and 8.6g of acrylic acid was added at a constant rate over 5 hours. A solution of ammonia, (5.0g in 300g of water), was added over 5 hours and the remaining sodium persulphate solution was added over 5 hours 30 minutes. Ethylene was charged to the reactor during the first four hours of these additions to maintain the pressure at 62 bar. The temperature was maintained at 70°C throughout the slow additions and for a further 30 minutes. The temperature was reduced to 50°C and solutions of t-butylhydroperoxide, (3.6g in 70g of water), and sodium metabisulphite, (3.6g in 70g of water), were added over 30 minutes while cooling to 30°C. The emulsion was discharged from the reactor and filtered through 250 mesh nylon to remove coagulum. The resultant latex had a solids content of 52.59%, viscosity of 87 centipoise, and an ethylene content by infra-red analysis of 22.5%.

#### Example 6

A solution of 10.5kg of Synperonic NP30, (70% active), in 98kg of deionised water and a monomer mixture consisting of 7.0kg of vinyl acetate and 0.56kg of acrylic acid were charged to a 50 gallon reactor. The reactor was purged three times with nitrogen and once with ethylene. The reactor was charged with ethylene (12.5kg), to a pressure of 40 bar, then 15% of a solution of sodium persulphate, (0.92kg in 19kg of water), was added to the reactor. The temperature was raised to 70°C, and then allowed to exotherm to 75°C. At this temperature a monomer mixture consisting of 133kg of vinyl acetate, 3.0kg of N-(n-butoxymethyl)acrylamide and 0.88kg of acrylic acid was added at a constant rate over 5 hours. A solution of ammonia, (0.25kg in 18kg of water), was added over 5 hours and the



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remaining sodium persulphate solution was added over 5 hours 30 minutes. After 30 minutes a further 28kg of ethylene was charged to the reactor over 3.5 hours maintaining the pressure at less than 60 bar. The temperature was maintained at 75°C throughout the slow additions and for a further 30 minutes. The temperature was reduced to 50°C and solutions of t-butylhydroperoxide, (0.37kg in 6 kg of water), and sodium metabisulphite, (0.37kg in 6kg of water), were added over 30 minutes while cooling to 30°C. The emulsion was discharged from the reactor and filtered through 250 mesh nylon to remove coagulum. The resultant latex had a solids content of 55.38%, viscosity of 108 centipoise, and an ethylene content by infra-red analysis of 23.0%.

#### Example 7

A solution of 320g of Synperonic NP30, (70% active), and 12.4g of Perlankrol PA conc in 2700g of deionised water and a monomer mixture consisting of 220g of vinyl acetate and 1.4g of acrylic acid were charged to a 12 litre stainless steel reactor. Perlankrol PA is the ammonium salt of nonylphenol ethoxylate with 4 ethylene oxide units and one sulphate group, obtainable from Harcros Chemicals UK Limited. The reactor was purged twice with nitrogen and once with ethylene. The temperature was raised to 75°C while charging the reactor with ethylene to a pressure of 62 bar. 15% of a solution of sodium persulphate, (28g in 800g of water), was added to the reactor. A monomer mixture consisting of 4120g of vinyl acetate, 91.0g of N-(n-butoxymethyl) acrylamide and 26.6g of acrylic acid was added at a constant rate over 4 hours 30 minutes. A solution of ammonia, (7.0g in 800g of water), was added over 4 hours 30 minutes and the remaining sodium persulphate solution was

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added over 5 hours. Ethylene was charged to the reactor during the first three hours of these additions to maintain the pressure at 62 bar, adding a total of 1148g. The temperature was maintained at 75°C throughout the slow additions and for a further 30 minutes. The temperature was reduced to 50°C and solutions of t-butylhydroperoxide, (11.2g in 100g of water), and sodium metabisulphite, (7.3g in 100g of water), were added over 30 minutes while cooling to 30°C. The emulsion was discharged from the reactor and filtered through 250 mesh nylon to remove coagulum. The resultant latex had a solids content of 54.11%, viscosity of 230 centipoise, and an ethylene content by infra-red analysis of 21.3%.

#### Example 8

This Example used the procedure of Example 6, except that the surfactant solution originally charged to the reactor also contained 0.41kg of Perlankrol PA conc. The resultant latex had a solids content of 55.37%, viscosity of 83 centipoise, and an ethylene content by infra-red analysis of 23.1%.

#### Example 9

A solution of 103g of Synperonic NP30, (70% active), and 4.0g of Perlankrol PA conc. in 750g of deionised water and a monomer mixture consisting of 67g of vinyl acetate and 0.45g of acrylic acid were charged to a 4 litre stainless steel reactor. The temperature was raised to 30°C, then the reactor was purged twice with nitrogen and once with ethylene. The reactor was charged with ethylene to a pressure of 52 bar, and then heated to a temperature of 75°C. At this temperature 15% of a solution of sodium



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persulphate, (9.0g in 300g of water), was added to the reactor. A monomer mixture consisting of 1306g of vinyl acetate, 30.0g of N-(n-butoxymethyl) acrylamide and 8.6g of acrylic acid was added at a constant rate over 4 hours. A solution of sodium vinyl sulphonate (72g; 25% active), and ammonia, (2.3g), in 210g of water was added over 4 hours and the remaining sodium persulphate solution was added over 4 hours 30 minutes. Ethylene was charged to the reactor during the first 2 hours 30 minutes of these additions to maintain the pressure at 62 bar. The temperature was maintained at 75°C throughout the slow additions and for a further 30 minutes. The temperature was reduced to 50°C and solutions of t-butylhydroperoxide, (3.6g in 70g of water), and sodium metabisulphite, (3.6g in 70g of water), were added over 30 minutes while cooling to 30°C. The emulsion was discharged from the reactor and filtered through 250 mesh nylon to remove coagulum. The resultant latex had a solids content of 54.00%, viscosity of 91 centipoise, and an ethylene content by infra-red analysis of 21.2%.

#### Example 10

This is a comparative example using N-methylolacrylamide (NMA) as the cross-linker. A solution of 103g of Synperonic NP30, (70% active), 1.36g of ferric ion solution, (1.0% active), and 0.7g of formic acid in 750g of deionised water and a monomer mixture consisting of 67g of vinyl acetate and 0.45g of crotonic acid were charged to a 4 litre stainless steel reactor. The temperature was raised to 30°C, then the reactor was purged twice with nitrogen and once with ethylene. The reactor was charged with ethylene to a pressure of 57 bar. A monomer mixture consisting of 1274g of vinyl acetate and 8.45g of crotonic acid and a solution of 120g of N-methylolacrylamide, (45% aq.), and 5.0g of

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ammonia in 205g of water were added at a constant rate over 5 hours. Initiator solutions comprising 7.2g of ammonium persulphate in 300g of water and 2.2g of formosul in 300g of water were added at double rate for 20 minutes, normal rate for 4 hours 20 minutes and double rate for 1 hour to give a total addition time for initiators of 5 hours 40 minutes. The temperature was slowly raised to 60°C during the first 3 hours of additions and maintained until the monomer addition was complete, then it was raised to 70°C until the initiator additions were complete. The temperature was reduced to 50°C and solutions of t-butylhydroperoxide, (3.6g in 35g of water), and sodium metabisulphite, (3.6g in 35g of water), were added over 30 minutes while cooling to 30°C. The emulsion was discharged from the reactor and filtered through 250 mesh nylon to remove coagulum. The resultant latex had a solids content of 49.70%, viscosity of 470 centipoise and an ethylene content by infra-red analysis of 20.5%.

Tensile strengths and formaldehyde levels of substrates impregnated with the products at Examples 1 to 10 were determined as described above, and the results are given in Tables 1 and 2.

It will be seen that products using NBMA as cross-linker give impregnated substrates with strengths generally comparable to those of substrates impregnated with products using NMA as cross-linker (Examples 4 and 10), while having substantially reduced formaldehyde levels.

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Table 1 Tensile Strengths and Formaldehyde Levels of  
Substrates Impregnated with Examples 1-4.

Example	1	2	3	4
<b>Filter Paper:</b>				
F dry (N)	162	164	166	165
F wet (N)	60	58	71	69
F solvent (N)	32	32	25	34
e dry (%)	6.2	6.0	5.9	6.5
e wet (%)	7.6	3.4	4.4	4.8
e solvent (%)	1.3	0.8	1.0	1.3
<b>Viscose web:</b>				
F dry (N)	30.3	24.1	30.8	26.4
F wet (N)	10.3	8.3	12.4	15.8
F solvent (N)	7.9	4.6	11.9	6.9
e dry (%)	23	36	17	37
e wet (%)	15	29	14	23
e solvent (%)	15	4	4	5
<b>Formaldehyde:</b>				
paper (ppm)	11	6	7	122
viscose (ppm)	*	10	12	118

\* = not measured

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Table 2 Tensile Strengths and Formaldehyde of Substrate  
Impregnated with Examples 5-10.

Example	5	6	7	8	9	10
Viscose:						
F dry (N)	6.4	6.2	5.8	6.0	7.3	8.1
F wet (N)	3.1	3.5	2.1	3.6	3.1	3.7
F solvent (N)	1.5	1.4	1.4	1.5	1.3	2.2
e dry (%)	28	30	52	29	43	29
e wet (%)	22	18	13	24	19	22
e solvent (%)	6	4	33	5	5	6
Formaldehyde:						
paper (ppm)	*	5	nd	nd	6.8	69

\* = not measured

nd = not detectable.

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Claims:

1. A binding composition for non-woven fibrous materials, comprising a copolymer emulsion in which at least about 30% by weight of the monomer content is vinyl C1 to C4 alkanoate and an amount of N-(n-butoxymethyl) acrylamide effective to act as a post polymerisation cross-linking agent is present.
2. A composition according to claim 1, wherein the amount of N-(n-butoxymethyl) acrylamide is in the range 0.5% to 10% by weight of the total monomer content.
3. A composition according to claim 2, wherein the amount of N-(n-butoxymethyl) acrylamide is less than about 5% by weight of the total monomer content.
4. A composition according to claim 1, 2 or 3, wherein not more than about 90% by weight of the monomer content is vinyl C1 to C4 alkanoate.
5. A composition according to any one of the preceding claims, wherein the vinyl C1 to C4 alkanoate comprises vinyl acetate.
6. A composition according to any one of the preceding claims, wherein the copolymer emulsion includes a C2 to C4 alkylene monomer.
7. A composition according to claim 6, wherein the C2 to C4 alkylene monomer is ethylene.

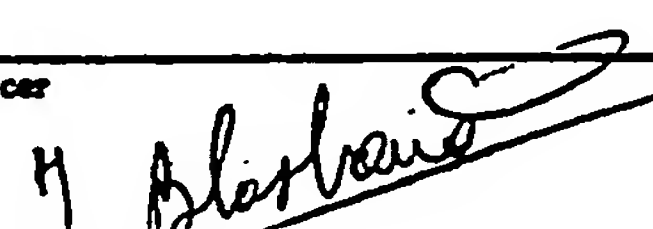
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8. A composition according to any one of the preceding claims, wherein the copolymer emulsion includes an alkyl (C2 to C10) (meth) acrylate.
9. A composition according to any one of the preceding claims, wherein the copolymer emulsion includes sodium vinyl sulphonate.
10. A process of binding a non-woven fibrous material, comprising impregnating the material with a binding composition in accordance with any one of the preceding claims; drying the copolymer emulsion; and subjecting the impregnated material to thermal treatment to provide cross-linking.
11. A non-woven fibrous material comprising a mass of fibres bound together by use of the binding composition of any one of claims 1 to 9.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 91/02002

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D04H1/64		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	D04H	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 147 759 (THE B.F. GOODRICH CO.) 10 July 1985 see page 3, line 20 - page 17, line 1; claims 1,2,6,7	1-4,8,10,11
A	EP,A,0 264 869 (THE B.F. GOODRICH CO.) 27 April 1988 see page 3, line 43 - page 8, line 21; claims 1,3,9,10,13	1-11
A	GB,A,1 177 199 (E.I. DU PONT DE NEMOURS AND CO.) 7 January 1970 see page 1, line 75 - page 5, line 3; claims 1,3,8,12,13,20	1-7
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
04 FEBRUARY 1992	18. 02. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	BLASBAND I. 	



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. GB 9102002  
SA 53175**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 04/02/92

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		JP-A- 60155778	15-08-85
		US-A- 4617230	14-10-86
EP-A-0264869	27-04-88	AU-B- 612600	18-07-91
		AU-A- 7959687	21-04-88
		JP-A- 63165563	08-07-88
		US-A- 4929495	29-05-90
GB-A-1177199	07-01-70	BE-A- 720123	28-02-69
		DE-A- 1794034	14-10-71
		FR-A- 1578624	14-08-69
		NL-A- 6810687	25-10-68

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82